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# Characterization of Advanced Sorbents for Dry SO2 Control

Acurex Corp., Research Triangle Park, NC

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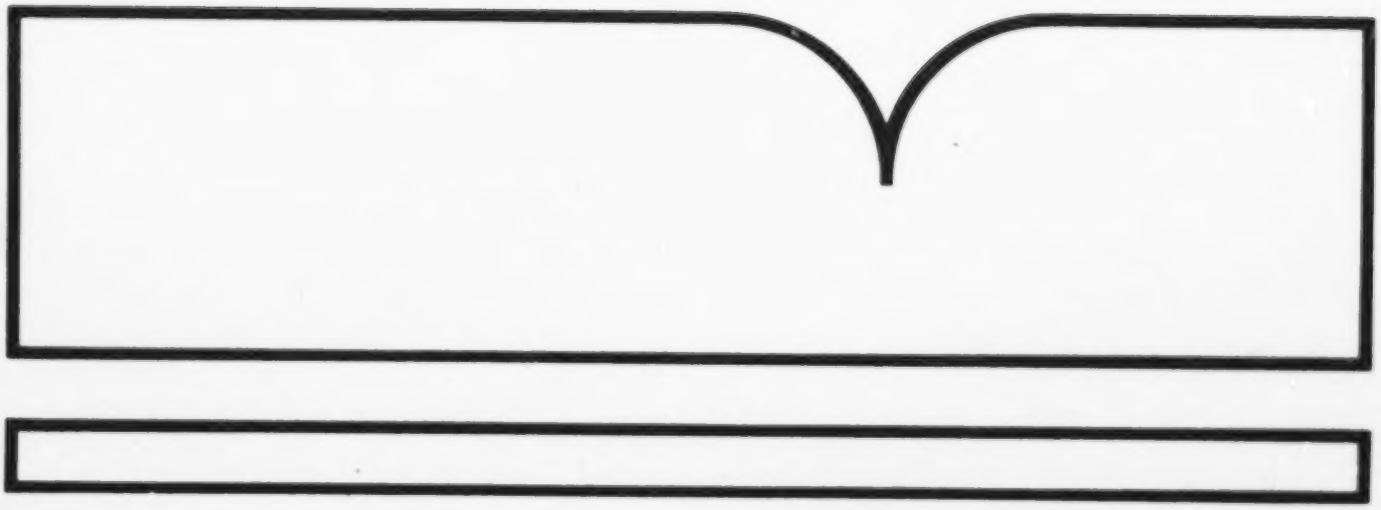

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# CHARACTERIZATION OF ADVANCED SORBENTS FOR DRY $SO_2$ CONTROL

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16. ABSTRACT The paper discusses the development of new flyash/lime sorbents for removing SO2 from coal-fired flue gas. Flyash/lime weight ratios of 1:1 to 10:1 and several additives to these sorbents for promoting their reactivity were evaluated in a bench-scale reactor simulating conditions in a fabric filter. Of the additives tested, Na2HPO4·7H2O, (NH4)2HPO4, and H3PO4 significantly enhanced the reactivity of the dry sorbents with SO2. Alternative sources of silica were reacted with lime, and the resultant dry sorbents were shown to be highly reactive with SO2. Of the siliceous materials tested, several diatomaceous earths, montmorillonitic clays, and kaolins were identified as containing reactive silica. The morphology of the sorbents developed was characterized. This information, along with the reactor test results, was used to rate the sorbents for pilot plant evaluation.

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| Sorbents | Combustion | Stationary Sources | 11G | |
| Sulfur Dioxide | Silicon Dioxide | Dry $SO_2$ Control | 07B | |
| Fly Ash | Filters | Fabric Filters | 21B | 14G |
| Calcium Oxides | Fabrics | | | 11E |
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ABSTRACT

New flyash/lime sorbents were developed for removing $SO_2$ from coal-fired flue gas. Flyash-to-lime weight ratios of 1:1 to 10:1 and several additives to these sorbents for promoting their reactivity were evaluated in a bench-scale reactor simulating conditions in a fabric filter. Of the additives tested, $Na_2HPO_4 \cdot 7H_2O$, $(NH_4)_2HPO_4$, and $H_3PO_4$ significantly enhanced the reactivity of the dry sorbents with $SO_2$. Alternative sources of silica were reacted with lime, and the resultant dry sorbents were shown to be highly reactive with $SO_2$. Of the siliceous materials tested, several diatomaceous earths, montmorillonitic clays, and kaolins were identified as containing reactive silica.

The morphology of the sorbents developed was characterized. This information, along with the reactor test results, was used to rate the sorbents for pilot plant evaluation.

## INTRODUCTION

New silica-enhanced lime sorbents were developed as part of EPA-funded work to develop retrofittable, low cost flue gas cleaning technology for controlling emissions associated with acid rain. Recently, this technology has included five basic processes: injection of dry sorbent into the furnace, dry sorbent injection into the gas-side of the economizer, in-duct dry sorbent injection, in-duct spray drying, and combined electrostatic precipitator (ESP)/fabric filter sorbent injection [1]. Direct injection of dry sorbents into the furnace and in-duct dry sorbent injection into flue gas offer low capital costs, because these methods do not require the costly atomizers, slurry preparation system, or solids dewatering equipment needed for other processes. Usually, long sorbent/gas contact times, such as those provided by the fabric filter cake, are needed for a dry sorbent to efficiently react with $SO_2$. New sorbents, with higher reactivity than conventional lime, were needed to increase the low $SO_2$ capture normally obtained with lime after its injection into the ductwork at plants with ESPs. ESPs have a shorter gas/sorbent contact time than do fabric filters, but have wide industrial application.

Recent tests by EPRI [2], using sorbent prepared by EPA's Air and Energy Engineering Research Laboratory (AEERL), indicated the superior performance of this sorbent over conventional $Ca(OH)_2$ in the duct/ESP system when steam was injected with the sorbent. Preliminary results showed that, at a stoichiometric ratio (moles Ca/mole $SO_2$) of about 2 and an 11°C (20°F) approach to adiabatic saturation, the sorbent prepared from flyash and $Ca(OH)_2$

at a weight ratio of 3:1 removed 55% $SO_2$ compared with 45% $SO_2$ removed with hydrated lime. These results agreed with those for flyash/$Ca(OH)_2$ sorbents which have been extensively tested in AEERL's facilities in Research Triangle Park (RTP) [3] and showed their performance to be significantly better than that of hydrated lime.

This paper describes the bench-scale evaluation of additives for increasing the reactivity of silica-enhanced lime sorbents. These enhanced sorbents were produced at flyash-to-lime weight ratios from 1:1 to 10:1 or with silica from sources other than flyash.

The siliceous material-to-lime weight ratio is used throughout this paper, rather than the molar ratio of silica-to-calcium, because the former is more useful in applying bench-scale results (e.g., scale-up). All siliceous materials considered are composites, and they may contain different amounts of silica available (active silica) for the reaction with lime. The molar ratio of silica-to-calcium does not directly indicate the amount of the siliceous material (active silica plus inerts) needed to activate a unit amount of lime as does the weight ratio (i.e., different amounts of siliceous materials with different $SiO_2$ content would be needed to obtain constant molar ratio of silica-to-calcium when activating a unit amount of lime).

## EXPERIMENTAL

### APPARATUS

The reactivity of sorbents was evaluated in a "sand-bed reactor" designed to simulate the conditions in a fabric filter. The experimental apparatus, shown in Figure 1, has been explained in detail elsewhere [4,5] and served to screen sorbents to be used in pilot plant studies. The reactor uses 1 g of a dry powdered reagent dispersed in 40 g of sand. Each sample is contacted with a $SO_2$-containing nitrogen stream under controlled temperature and relative humidity (i.e., a controlled approach to the adiabatic saturation

temperature). One hour has been arbitrarily selected as the residence time of the sorbent in the reactor while exposed to the $SO_2$-containing gas stream. Prior to each 1-h run, the sorbent/sand mixture in the reactor was exposed for 1 h to the temperature and relative humidity at which the test was to be performed. This procedure allowed the simulation of the "moisture history" of the dry sorbent injected into the duct and later humidification of the gas as differentiated from the procedure described elsewhere [6] which simulated the "moisture history" of the spray-dried sorbent in a duct or absorber.

The screening experiments were performed at 64°C (147°F) and a relative humidity of 60% [corresponding to an approach to saturation, $\Delta t_s$, of 10°C (18°F)]. Some tests were performed in the range from 30 to 80% relative humidity [corresponding to a $\Delta t_s$ range from 20 to 4.4°C (36 to 8°F)]. The $SO_2$ concentration was normally 1.33 or 2.67 g/m$^3$ (500 or 1000 ppm) at 20°C (68°F).

## SAMPLE PREPARATION AND EVALUATION

Sample preparation consisted of batch atmospheric hydration of the silica material/lime mixture followed by drying. These procedures are described in detail elsewhere [3]. The reactivity of the sorbents toward $SO_2$ is expressed in this paper as "conversion" or "$SO_2$ capture." Conversion is defined as the ratio of the total number of mols of $SO_2$ reacted after 1 h to the number of mols of $Ca(OH)_2$ initially in the sorbent. $SO_2$ capture is defined as the total number of mmols of $SO_2$ reacted after the 1-h exposure period per 1 g of sorbent. The reactivity of reagent grade $Ca(OH)_2$ (Fisher C-97) for a residence time of 1 h in the sand bed reactor was established as the baseline for all work reported here. Using simulated flue gas containing 1000 ppm $SO_2$ at a temperature of 64°C and 60% relative humidity [$\Delta t_s$ = 10°C (18°F)], 1 g of reagent grade $Ca(OH)_2$ resulted in a conversion of 0.17 mol $SO_2$/mol $Ca(OH)_2$ and an $SO_2$ capture of 2.1 mmol $SO_2$/g $Ca(OH)_2$ after a 1-h exposure.

The morphology of the samples was characterized using a scanning electron microscope (SEM). The composition of the particles was measured by an x-ray microprobe, and the crystalline phases were detected with an x-ray diffractometer. The nitrogen B.E.T. surface area was analyzed using an automated analyzer.

## SOURCES OF SILICA FOR REACTION WITH LIME

The most obvious and abundant source of silica in power plants is flyash generated from the combustion of coal. The reaction of flyash (or other siliceous material) with lime in the presence of water is called a pozzolanic reaction and is discussed elsewhere [5]. As a result of this reaction, calcium-aluminum-silicate hydrates are formed. At temperatures from 20 to about 100°C (68 to 212°F), the calcium silicates synthesized are primarily in two forms: silicate hydrate and dicalcium silicate hydrate (of alpha, beta, or gamma type). The $CaO$-$SiO_2$-$Al_2O_3$-$H_2O$ system is very complicated, especially with flyash present, because the glass composition varies even between individual particles of the same flyash [7]. The pozzolanic activity of an ash (i.e., ability to combine with lime in water solution) is proportional to its surface area and can be further increased by grinding [8], which breaks the glassy layer on a flyash particle and facilitates flyash dissolution. The surface area has little dependence on particle size of the flyash but usually is larger for bigger particles [9].

Cryptocrystalline forms of silica and aluminosiliceous clays were considered as important alternate sources of silica in addition to flyash. Cryptocrystalline forms of silica tested included: diatomaceous earth, tripoli, and pumice. Diatomaceous earth (diatomite, kieselgur) is a sedimentary rock composed of siliceous shells of a flowerless plant of the class Bacillarieae. Initially, silica in diatomaceous earth was amorphous; but, since many of the known deposits are millions of years old, the silica

may be present as cryptocrystalline quartz. Initial results of tests using several commercial grades of diatomaceous earth were published earlier [3]. Tripoli and pumice, other forms of microcrystalline silica, are of volcanic origin [10]. Their properties should be similar to the high surface area amorphous silica mined at Pozzouli, Italy, during the Roman Empire. Even today, Italian pozzolans are mined and widely used as a concrete admixture for their superior ability (relative to flyash) to combine with free lime [11].

Clay is very abundant in the earth's crust. It is fine-grained and composed of a group of crystalline minerals known as clay minerals. These minerals are hydrous silicates, and some contain iron, alkalies, and alkaline earths [12]. The U. S. Bureau of Mines classifies clays into six groups: kaolin, ball clay, fire clay, bentonite, Fuller's earth, and common clay and shale. Of these kaolin and bentonite may be of interest in flue gas desulfurization (FGD). Ball clay and fire clay are mainly kaolinite, a kaolin mineral. Fuller's earth contains distinct needle-shaped attapulgite; therefore, it may possess environmentally unacceptable asbestos-like properties. Kaolinite may be formed by weathering of potassium and sodium-feldspars, and consists of distinct layers of silica and aluminum. Its general chemical formula is $Al_2(OH)_4Si_2O_5$; however, kaolinite may have Mg and/or Fe intrusions. Conventionally, it is used as a raw ceramic material, as well as a filler in the paint, paper, and rubber industries.

Bentonite is a rock composed largely of montmorillonite from the montmorin group of minerals. Montmorillonite consists of successive layers, each formed by one Al sheet enclosed between two Si sheets [13]. When exposed to $H_2O$, montmorillonite swells considerably because of its large surface area (400-800 $m^2/g$), the large number of exchangeable cations ($Na^+$, $Ca^{++}$), and the poor ordering of several layers. The general formula of montmorillonite is $(Al, Mg, Na, Fe)_{2x}(OH)_{2x}Si_4O_{10}xnH_2O)$, where n (the number of molecules of

water) varies depending on the clay's source. Sometimes clays are activated with acids which solubilize structural cations and open the clay structure to increase surface area. It has been shown that a reaction of $Ca(OH)_2$ with clays at room temperature [20°C (68°F)] and at 39°C (102°F) gives tetracalcium aluminate hydrates and silicates among other products [14].

Deposits of natural clay are abundant; in 1983 almost 41 million tonnes (45.2 million tons) was sold in the U.S. [15]. Out of this total, 3 million tonnes (3.3 million tons) were bentonite and 7 (7.7) million were kaolin. While deposits of common clay and shale are widespread over all the U.S., kaolins are found predominately in the East (Georgia, South Carolina) and bentonites in the West (California, Wyoming). Some bentonites are also found in Texas, Nevada, and Mississippi.

FLYASH/$Ca(OH)_2$ SORBENTS

It was observed previously [3,6] that the conversion of $Ca(OH)_2$ increased with increased weight ratio of flyash to $Ca(OH)_2$. Flyash-to-$Ca(OH)_2$ weight ratios ranging from 1 to 10 were investigated during the current work. Flyash from the Clinch River Power Plant in Carbo, VA, obtained from the burning of eastern bituminous coal, was the silica source. Some experiments were also performed using flyash from the San Miguel Electric Cooperative plant near San Antonio, TX, which burned Texas lignite. Figure 2 shows the reactivity of the sorbent as a function of flyash-to-$Ca(OH)_2$ weight ratio, with the left-hand ordinate giving the conversion of $Ca(OH)_2$ and right-hand ordinate giving the $SO_2$ capture. All samples tested were prepared by slurrying at 90°C (194°F) for 8 h at a water-to-solids ratio of 15:1 (6% solids in the slurry). The samples were then dewatered and dried. The resulting dry powdered sorbent (1 g) was mixed with sand (40 g) and exposed to 500 ppm $SO_2$ for 1 h in the sand-bed reactor operated at 64°C (147°F) and 60% relative humidity [$\Delta t_s$ = 10°C (18°F)]. Figure 2 shows that the conversion of $Ca(OH)_2$ in the sorbent

increased while $SO_2$ capture decreased with increasing flyash-to-$Ca(OH)_2$ weight ratio. The measured B.E.T. surface area of the samples increased with increasing weight ratio of flyash-to-$Ca(OH)_2$: 9.9 and 19.2 $m^2/g$ for samples with ratios of 2 and 10, respectively. There was no difference in the reactivity for a given flyash-to-$Ca(OH)_2$ weight ratio when flyash from either lignitic or bituminous coal was used despite the respective flyashes having markedly different alkaline material compositions. Based on these results and the practical need to limit the solids loading of the particulate collector, flyash/$Ca(OH)_2$ mixtures prepared at weight ratios of 3 and 5 were recommended for pilot plant testing in AEERL's 100 $m^3/h$ (58 cfm) spray dryer/baghouse or humidification/dry injection/baghouse system.

An economic evaluation of an AEERL-proposed post-combustion flue gas cleaning process (consisting of in-duct injection of dry sorbent into humidified flue gas) indicated that the sorbent preparation cost could have significant impact on the overall costs of the process. A major part of the sorbent preparation costs would be the cost of removing water from $Ca(OH)_2$ slurried with flyash.

Since the water-to-solids ratio routinely used for preparing sorbents for the sand-bed experiments was 15:1, decreasing the amount of water used during the slurrying step of sorbent preparation could reduce the cost of the process. Testing was performed to evaluate the effect of the water quantity used during slurrying on the reactivity of the sorbent in the sand-bed reactor. The results, presented in Figure 3, differ over three distinct subranges of the slurry solids content (total range of 4.5 - 80% solids) for the sorbent prepared with the flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1 (flyash-to-CaO weight ratio of 3:1) and slurrried at 90°C (194°F) for 8 h. Dry sorbents prepared this way were tested in the sand-bed reactor operated at 64°C (147°F), 60% relative humidity [$\Delta t_s$ = 10°C (18°F)], and $SO_2$ concentration

of 500 ppm. Based on the curve in Figure 3, the conversion of sorbents in the sand-bed reactor was 0.37 and 0.28 mol $SO_2$/mol $Ca(OH)_2$ for the subranges of 5-10 and 20-80% solids in the slurry during sorbent preparation, respectively. Conversion decreased from 0.37 to 0.28 mol $SO_2$/mol $Ca(OH)_2$ in the intermediate range of 10-20% solids in the slurry during sorbent preparation. The solids concentration of 50-80% corresponded to a thick paste, which was very hard to mix thoroughly. By utilizing equipment specifically designed to handle thick pastes (e.g., ribbon blenders, Nauta blenders), therefore providing better mixing of $Ca(OH)_2$ and flyash, higher reactivity sorbents (possibly equal to those prepared by slurrying at a low solids percent) might be achieved.

FLYASH/$Ca(OH)_2$ SORBENTS WITH ADDITIVES

Only moderate sorbent enhancement [about 125% greater $SO_2$ capture than with $Ca(OH)_2$ alone] occurred when flyash and $Ca(OH)_2$ were slurried at a weight ratio of 2.3:1, even at high temperature. Higher flyash/$Ca(OH)_2$ weight ratios were needed to make the enhancement more pronounced. Unfortunately, high ratios of flyash-to-$Ca(OH)_2$, which may be achieved in commercial applications by increasing the recycle of sorbent, degrade the performance of ESPs because of increased solids loading.

One way to increase the reactivity of the flyash/$Ca(OH)_2$ sorbent, while keeping the weight ratio low, would be to use additives for increasing the dissolution rate of flyash, which is believed to be the rate limiting step in the formation of calcium silicate hydrates in the flue gas desulfurization (FGD) system. Tests investigating the effect of NaOH on the reactivity of sorbents formed at different slurrying conditions have been reported [3]: they seem to confirm the hypothesis that the reactivity of sorbents could be improved by increasing the dissolution rate of flyash by adding NaOH.

Recently the earlier work with NaOH was expanded and included testing of the effect of the absolute amount of NaOH additive on the reactivity of

flyash/$Ca(OH)_2$ sorbent prepared at the weight ratio of 2.3:1 and slurried at 90°C (194°F) for 8 h. Two levels of NaOH concentration (0.1 and 0.25 N) were maintained during this study. The results are presented in Figure 4. In this study a maximum in sorbent conversion occurred at about 4 mol % of NaOH additive [$Ca(OH)_2$-based]. This sorbent was slurried for 8 h at 90°C (194°F) and had a weight ratio of flyash-to-$Ca(OH)_2$ of 2.3:1. After drying, it was exposed to 500 ppm $SO_2$ in the sand-bed reactor, and its conversion reached an experimental maximum of 0.55 mol $SO_2$/mol $Ca(OH)_2$ when the concentration of NaOH was 0.25 N. Lowering the concentration of NaOH to 0.1 N, by increasing the amount of water added to the sample, decreased the conversion to 0.45 mol $SO_2$/mol $Ca(OH)_2$.

Assuming that the flyash used was about 50% silica, the data in Figure 4 appear to be consistent with data on the production of α-dicalcium silicate hydrate [16]. Reference 16 indicated 6.7 mol % NaOH as the optimum amount for the formation of α-dicalcium silicate hydrate when CaO was hydrated with diatomaceous earth at a diatomaceous earth/CaO weight ratio of 1.9:1. α-dicalcium silicate hydrate is probably the most reactive silicate with $SO_2$.

Three other additives tested for enhancing the reactivity of the sorbent prepared at a weight ratio of flyash-to-$Ca(OH)_2$ of 2.3:1 were $Na_2HPO_4 \cdot 7H_2O$, $(NH_4)_2HPO_4$, and $H_3PO_4$. Phosphates were reported [17, 18] to facilitate the breaking and dissolution of the glassy layer of flyash, increasing its pozzolanic activity and the overall amount of silicates produced in the system. Additionally, phosphates are known to be good dispersing agents [19], which prompted testing of both $Ca(OH)_2$ and CaO as sources of lime.

The results of tests employing sodium and ammonium phosphates and phosphoric acid, shown in Figure 5, give the conversion as a function of the absolute amount of phosphate added for both $Ca(OH)_2$ and CaO [5 g of flyash with 2.2 g of $Ca(OH)_2$ or 5 g of flyash with 1.67 g CaO; i.e., the

flyash-to-CaO weight ratio was 3:1 in both cases]. All data in Figure 5 were obtained for sorbent prepared by slurrying flyash with lime at 90°C (194°F) for 8 h and, after drying, exposing the dry sorbent to 500 ppm $SO_2$ in the sand-bed reactor operated at 64°C (147°F) and 60% relative humidity [$\Delta t_s$ = 10°C (18°F)]. The maximum conversions obtained with flyash/$Ca(OH)_2$ sorbents were achieved when 4 mol % of either sodium or ammonium phosphate was added. With $H_3PO_4$ as the additive, the maximum conversion was when 5 mol % was added. These results suggest that the enhanced conversion of $Ca(OH)_2$ was probably due to the increased dissolution of flyash resulting from the presence of $PO_4$ ion and, consequently, the increased formation of calcium silicate hydrates. It was also observed that, when CaO instead of $Ca(OH)_2$ was slurried with flyash the amount of phosphate needed to reach the same degree of reactivity was 50% and 70% when $(NH_4)HPO_4$ and $Na_2HPO_4 \cdot 7H_2O$ were used, respectively. For example, a maximum conversion of 0.5 mol $SO_2$/mol $Ca(OH)_2$ was reached when 4 and 8 mol % of $(NH_4)_2HPO_4$ were added during the slurrying of flyash with CaO and $Ca(OH)_2$, respectively. This result may stem from the dispersing properties of phosphates, present during the hydration of CaO, thereby resulting in finer particles in the product [as compared to the product obtained using $Ca(OH)_2$]. These smaller particles would more easily react with silica from the flyash to form calcium silicate than would the coarser $Ca(OH)_2$ particles.

Finally, parametric tests were run to investigate the effect of relative humidity on the reactivity of flyash/$Ca(OH)_2$ sorbent prepared at the weight ratio of 2.3:1 with and without additive. Two sorbents were compared: one was slurried at 90°C (194°F) for 24 h, while the second was slurried at 90°C for only 8 h but with 4 mol % of NaOH additive. The results are presented in Figure 6 along with those for a reagent grade $Ca(OH)_2$ for comparison. The reactivity of the sorbent prepared with NaOH additive is clearly higher at high humidities than the reactivity of sorbent slurried at 90°C for 24 hours

without the additive. The final conversions were 0.54 and 0.51 mol $SO_2$/mol $Ca(OH)_2$ when fly ash/$Ca(OH)_2$ sorbents prepared with and without NaOH, respectively, were exposed to 500 ppm $SO_2$ in the sand-bed reactor operating at 60% relative humidity ($\Delta t_s$ = 10°C). At 80% relative humidity in the reactor ($\Delta t_s$ = 4°C), the corresponding conversions were 0.76 and 0.67 mol $SO_2$/mol $Ca(OH)_2$. The increasing difference in the reactivity of the two discussed sorbents with the increasing relative humidity would be expected due to the deliquescent properties of NaOH. When the relative humidity is higher than about 50%, the NaOH absorbs water in addition to the sorbent itself, while at lower relative humidity the sorbent alone absorbs water. Thus, at the higher relative humidity, the reactivity of the sorbent with a deliquescent additive is increased.

SCREENING OF ALTERNATE SOURCES OF SILICA

All samples for the screening tests were prepared by slurrying the silica-bearing material with CaO at a weight ratio of 1:1 for 4 h at 90°C. Dry samples were exposed to 1000 ppm $SO_2$ in the sand-bed reactor operating at 60% relative humidity ($\Delta t_s$ = 10°C) and 64°C. The first group of minerals tested were cryptocrystalline silica materials including: diatomaceous earths, pumices, and tripolis. The properties of siliceous promoters, as well as the reactivities of sorbents prepared using them, are shown in Table 1. Only three natural grade diatomaceous earths are listed in Table 1, since such earths are discussed in greater detail elsewhere [3]. As can be seen, diatomaceous earths were very effective promoters of the reactivity of $Ca(OH)_2$. Generally, the weaker effect for pumices and tripolis is probably a result of the slurrying conditions. These materials should be better crystallized than the diatomaceous earths; therefore, they would require longer slurrying periods than were used for the screening tests. The conversion of the cryptocrystalline silica-promoted sorbents tested in the

screening series correlates rather well with the B.E.T. surface area, with conversions increasing proportionally with increasing surface area. An example of the well developed surface area of the sorbent prepared by slurrying diatomaceous earth (MN-53 from Eagle-Picher) with CaO at the weight ratio of 1:1 at 90°C for 4 h is shown photographically in Figure 7. This sorbent was very reactive with $SO_2$ in the sand-bed reactor, and the observed conversion of $Ca(OH)_2$ (when exposed to 1000 ppm $SO_2$ at 64°C and 60% relative humidity) was 0.84 mol $SO_2$/mol $Ca(OH)_2$.

Several grades of naturally occurring montmorillonitic clays and kaolins, as well as acid-activated bentonitic clays, were tested using the slurrying and sand-bed reactor conditions described above. The properties of clay promoters and reactivities of sorbents prepared using them are shown in Table 2. All clay additives increased the conversion of $Ca(OH)_2$ and the $SO_2$ capture by the sorbents. Different degrees of activation were achieved when clays of similar composition were slurried with lime. The differences were probably caused by the varying crystallinity and physical properties of clays; it should be possible to overcome these differences by applying more stringent slurrying conditions and/or additives. However, the scope of the work reported here was to demonstrate the capability of clayey additives to promote the reactivity of $Ca(OH)_2$ with $SO_2$. This has been demonstrated. For example, adding Bentonite 149 (from Whittaker, Clark, & Daniels) to lime, followed by slurrying and testing under conditions noted above, resulted in a $Ca(OH)_2$ conversion of 0.76 mol $SO_2$/mol $Ca(OH)_2$ compared with the baseline of 0.17 mol $SO_2$/mol $Ca(OH)_2$ for reagent grade $Ca(OH)_2$. The best kaolin tested--ASP-400 from the Engelhard Corporation--yielded a conversion of $Ca(OH)_2$ of 0.54 mol $SO_2$/mol $Ca(OH)_2$ compared with the baseline value noted above.

The correlation of the reactivity with the measured B.E.T. surface area of the sorbent was not as evident with clays as it was with cryptocrystalline

silica. For example, sorbents prepared with Na-Ca-Montmorillonite (from Ward's Natural Science) and Volclay 325 (from American Colloid Company), which under the screening conditions demonstrated comparable conversions of 0.48 and 0.43 mol $SO_2$/mol $Ca(OH)_2$, revealed surface areas of 24 and 35 $m^2/g$, respectively. The surface area measured on the best performing sorbent produced with a clayey additive [Bentonite 149, with 0.76 mol $SO_2$/mol $Ca(OH)_2$ conversion] was also 24 $m^2/g$. This difficulty in correlating the reactivity with the surface area of clay-enhanced sorbents is probably due to the properties of clays which have very unstable structures upon contact with moisture. The increase of the interlayer spacing in clays with the increasing humidity of the surrounding gas is very material-specific. Thus, the samples of sorbents prepared with different clayey additives and exposed to the constant humidity in the sand-bed reactor of 60% ($\Delta t_s$ = 10°C) could have expanded to a different degree and exposed different surface areas for reaction with $SO_2$.

PARAMETRIC TESTS WITH ALTERNATE SOURCE SILICA-ENHANCED SORBENTS

Two of the screened clays, Bentonite 149 and ASP 400, were selected for parametric tests. The effect of the weight ratio of clay-to-CaO on the conversion of the prepared sorbent in the sand-bed reactor was studied; the results are shown in Figure 8. Both the conversion of $Ca(OH)_2$ and the $SO_2$ capture in the case of Bentonite 149/CaO sorbent peaked at a weight ratio of clay-to-CaO near 1:1. Also shown in Figure 8 is the reactivity for sorbent prepared by slurrying diatomaceous earth (MN-53)/CaO at different weight ratios.

An x-ray diffraction analysis was done for MN-53/CaO samples; the resulting correlation of $SO_2$ capture by the sorbent in the sand bed with the amount of $Ca(OH)_2$ detected is presented in Figure 9. As might be expected, the $SO_2$ capture (reactivity of the sorbent) increased with the decreasing amount

of $Ca(OH)_2$ detected in the sample. These results suggest that a new, more reactive phase was formed after slurrying diatomaceous earth (MN-53) with CaO for 4 h at 90°C, since usually the sample with the greatest initial amount of $Ca(OH)_2$ should remove the greatest $SO_2$ because conventional alumino-siliceous compounds are considered to be inert toward $SO_2$. The point in Figure 9 representing the sorbent with a $Ca(OH)_2$ intensity of 53 yielded an $SO_2$ capture of only 2.6 mmol $SO_2$/g of sorbent and is significantly below the other data. This point is believed to have been the result of incomplete hydration, as indicated by comparison with other test data. Also shown in Figure 9 is the correlation between the surface area developed after slurrying MN-53 with CaO at different weight ratios and $SO_2$ capture by the specific sorbent. Similarly to what was observed for all of sources of cryptocrystalline silica tested, the $SO_2$ capture (reactivity) increased with the increasing surface area of the sorb nts.

## CONCLUSIONS

- The ability of flyash, cryptocrystalline silica, and clayey materials to promote the reactivity of $Ca(OH)_2$ towards $SO_2$ has been demonstrated.
- The conversion of $Ca(OH)_2$ increased and the $SO_2$ capture decreased with increasing flyash-to-$Ca(OH)_2$ weight ratio. While this ratio varied from 1:1 to 10:1 in the present study, an earlier study showed the same trends for the ratio ranging from 10:1 to 21:1.
- The ability of flyash to react with $Ca(OH)_2$ in very concentrated slurries (up to 80% solids) has been demonstrated. This could be very important for minimizing cost via recycling of fly ash/partially spent sorbent in retrofitted $SO_2$ control applications.

- The gradual addition of $Ca(OH)_2$ (as with make-up lime during recycle) almost doubled $SO_2$ capture compared with the once-through pass of $Ca(OH)_2$.
- The reactivity of sorbents prepared at the weight ratio of flyash-to-$Ca(OH)_2$ of 2.3:1 increased with additives such as NaOH, $Na_2HPO_4 \cdot 7H_2O$, $(NH_4)_2HPO_4$, and $H_3PO_4$.
- The reactivity of the sorbents prepared by slurrying cryptocrystalline silica with CaO correlated with B.E.T. surface area, regardless of the source of silica or the weight ratio of siliceous material-to-lime tested. The reactivity increased with increasing surface area.
- Clayey additives were very effective promoters of the reactivity of $Ca(OH)_2$ after slurrying at elevated temperature (90°C) for a prolonged time (4 hours). There was no direct correlation between the B.E.T. surface area and reactivity of clay-enhanced sorbents.

## REFERENCES


1. Rhudy, R.G., M. McElroy, and G. Offen, Status of calcium-based dry sorbent injection $SO_2$ control. In: Proceedings: Tenth Symposium on Flue Gas Desulfurization, Atlanta, Georgia, November 1986; Vol. 2, EPA-600/9-87-004b, pp. 9-68-9-83, February 1987.

2. Blythe, G.M., V. Bland, C. Martin, M. McElroy, and R. G. Rhudy, Pilot-scale studies of $SO_2$ removal by the addition of calcium-based sorbents upstream of a particulate control device. Ibid, pp. 9-84--9-105, February 1987.

3. Jozewicz, W., C. Jorgensen, J.C.S. Chang, C.B. Sedman, and T.G. Brna, Development and pilot plant evaluation of silica-enhanced lime sorbents for dry flue gas desulfurization. Ibid, pp. 9-123--9-144, February 1987.

4. Jorgensen, C., J.C.S. Chang, and T.G. Brna, Evaluation of sorbents and additives for dry $SO_2$ removal. Paper presented at the AIChE Spring National Meeting, New Orleans, Louisiana. 1986. Accepted for publication in Environmental Progress.

5. Jozewicz, W., J.C.S. Chang, T.G. Brna, and C.B. Sedman, Reactivation of solids from furnace injection of limestone for $SO_2$ control. In: Proceedings: 1986 Joint Symposium on Dry $SO_2$ and Simultaneous $SO_2/NO_x$ Control Technologies, Vol. 2, EPA-600/9-86-029b, (NTIS PB87-120457), pp. 30-1--30-20, 1986.

6. Jozewicz, W. and G.T. Rochelle, Flyash recycle in dry scrubbing. Environmental Progress. 5,4:219, 1986.

7. Diamond, S., Particle morphologies in fly ash. Cement and Concrete Research. 16:569, 1986.

8. Raask, E. and M.C. Bhaskar, Pozzolanic activity of pulverized fuel ash. Cement and Concrete Research 5:363, 1975

9. Schure, M.R., P.A. Soltys, D.F.S. Natusch, and T. Mauney, Surface area and porosity of coal fly ash. Environmental Science and Technology. 19,1:82, 1985.

10. Meisinger, A.C., Pumice and pumicite. In: Bureau of Mines (ed.), Minerals Yearbook. U. S. Department of the Interior, pp. 709-11. 1983.

11. Sersabe, R. and G. Frigione, Natural zeolites as constituents of blended cements. La Chimica e L'Industria. 67,4:177, 1985.

12. Ampian, S.G., Clays. In: Bureau of Mines (ed.), Mineral facts and problems. Bulletin 671, U. S. Department of the Interior, pp. 183-97. 1980.

13. Grim, R.E., Clay Mineralogy. McGraw-Hill Book Company, Inc. New York, 1953.

14. Aardt, van J.H.P. and S. Visser, Calcium hydroxide attack on feldspars and clays: possible relevance to cement-aggregate reactions. Cement and Concrete Research. 7:643, 1977.

15. Ampian, S.G., Clays. In: Bureau of Mines (ed.), Minerals Yearbook. U. S. Department of the Interior, pp. 221-254. 1983.

16. Leineweber, J.P., Method of producing dicalcium silicate hydrate. U.S. Patent No. 3,131,024. 1964.

17. Santoro, L., O. Aletta, and G.L. Valenti, Hydration of mixtures containing flyash, lime and phosphogypsum. Thermochimica Acta. 98:71, 1986.

18. Bergeson, K.L., J.M. Pitt, and T. Demirel, Increasing cementitious products of a class C flyash. Transportation Research Record. 998:41, 1984.

19. Conley, R.F., Design, functionality, and efficiency of pigment dispersants in water-base systems. Journal of Paint Technology. 46:594:51, 1974.

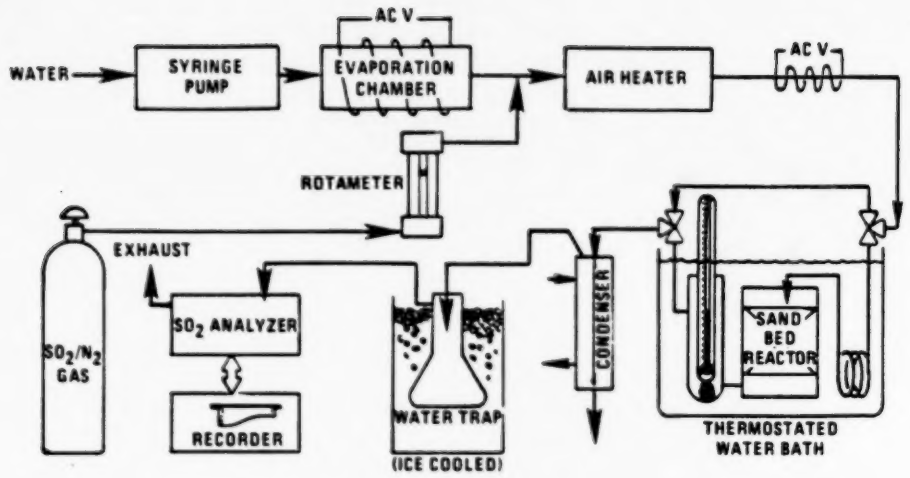


Figure 1. Experimental apparatus.

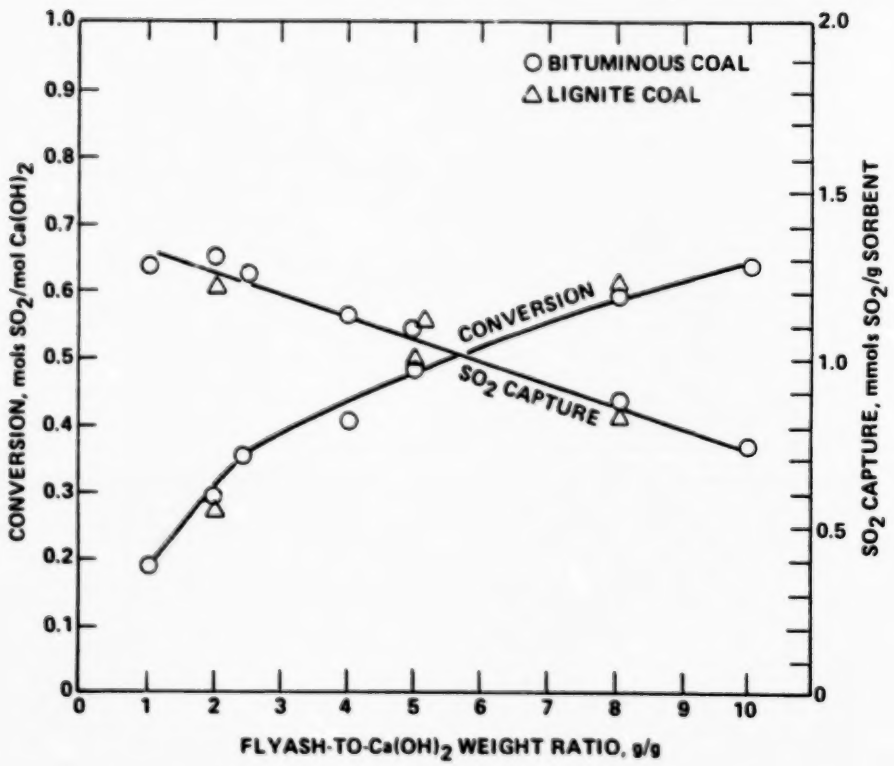


Figure 2. The effect of flyash-to-$Ca(OH)_2$ weight ratio during slurrying on the reactivity of dry sorbent in the sand-bed reactor (slurring: 8 h at 90°C; sand-bed conditions: 500 ppm $SO_2$, 60% relative humidity, 64°C).

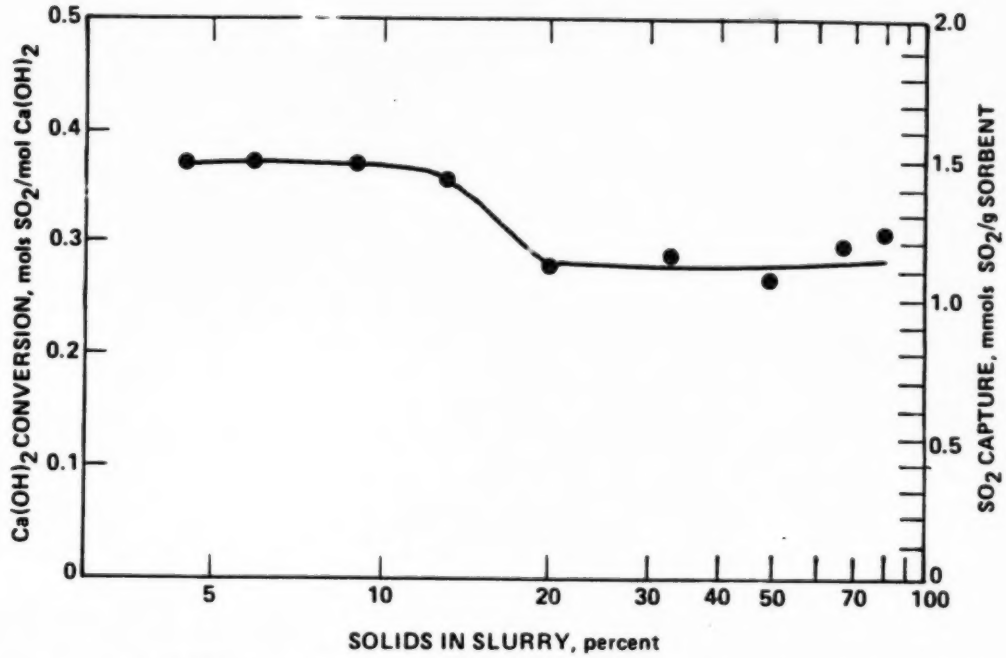


Figure 3. The ability of flyash to react with $Ca(OH)_2$ in slurries of different concentrations (slurrying: 8 h at 90°C; sand-bed conditions: 500 ppm $SO_2$, 60% relative humidity, 64°C).

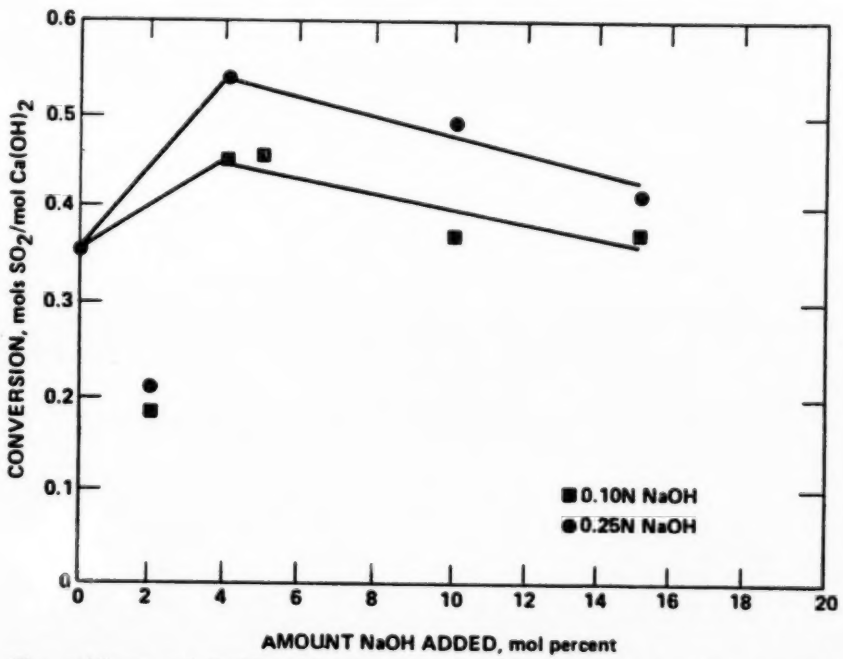


Figure 4. The effect of NaOH addition during slurrying on the reactivity of dry sorbent in the sand-bed reactor (slurrying and sand-bed conditions the same as in Figure 3).

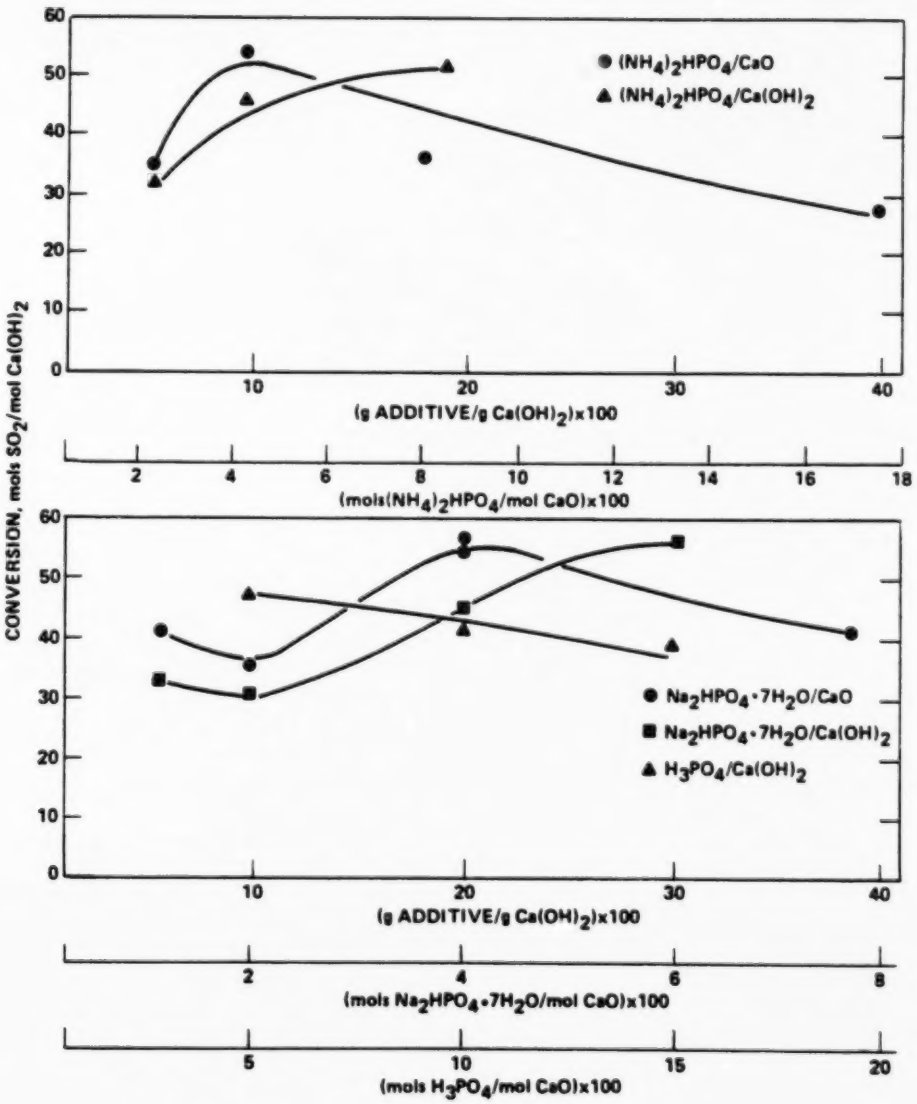


Figure 5. Reactivity enhancement of flyash/$Ca(OH)_2$ and flyash/CaO sorbents by use of additives (slurrying and sand-bed conditions same as in Figure 3).

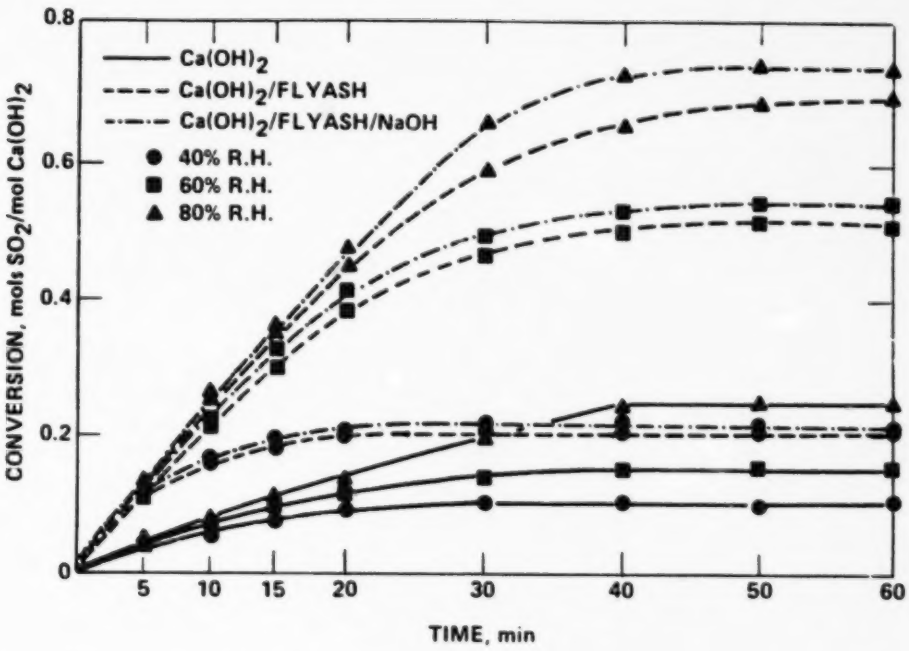


Figure 6. Combined deliquescent and flyash-digesting effect of NaOH (slurrying: 8 h at 90°C; sand-bed conditions: 500 ppm $SO_2$, 64°C, relative humidity as shown above).

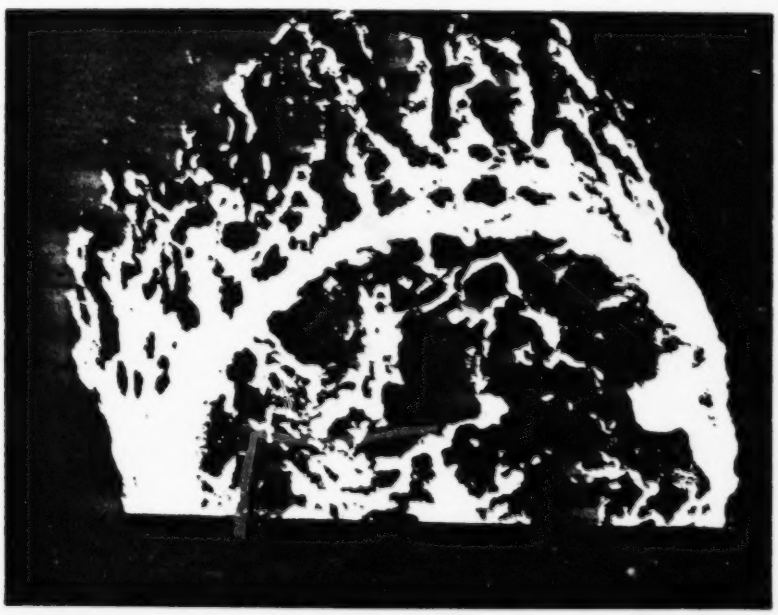

Figure 7. SEM photograph (10,000x) of diatomaceous earth (MN-53)/CaO sorbent (weight ratio = 1:1) slurried at 90°C for 4 h.

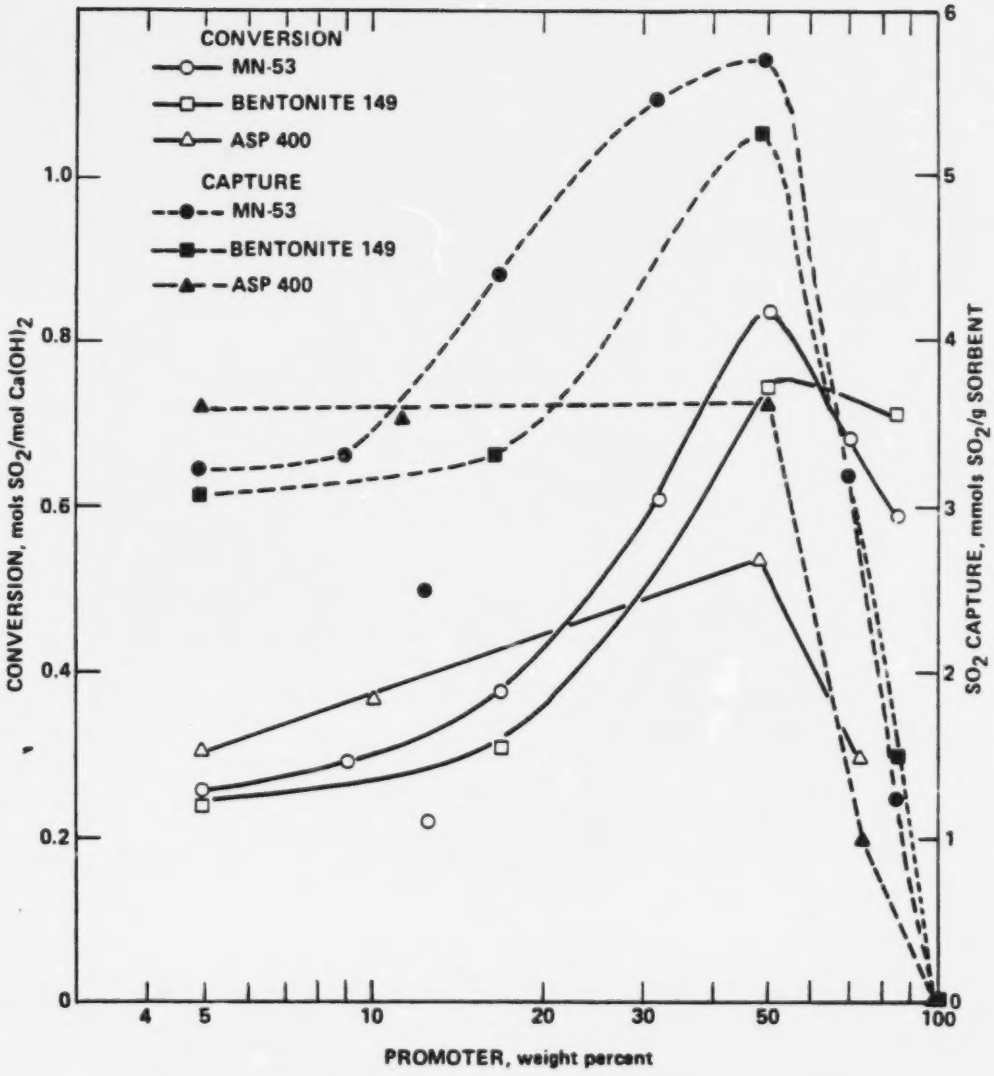


Figure 8. The effect of the weight ratio of siliceous material/lime on the reactivity of the sorbent in the sand-bed reactor (slurrying: 4 h at 90°C; sand-bed conditions: 1000 ppm $SO_2$, 60% relative humidity, 64°C).

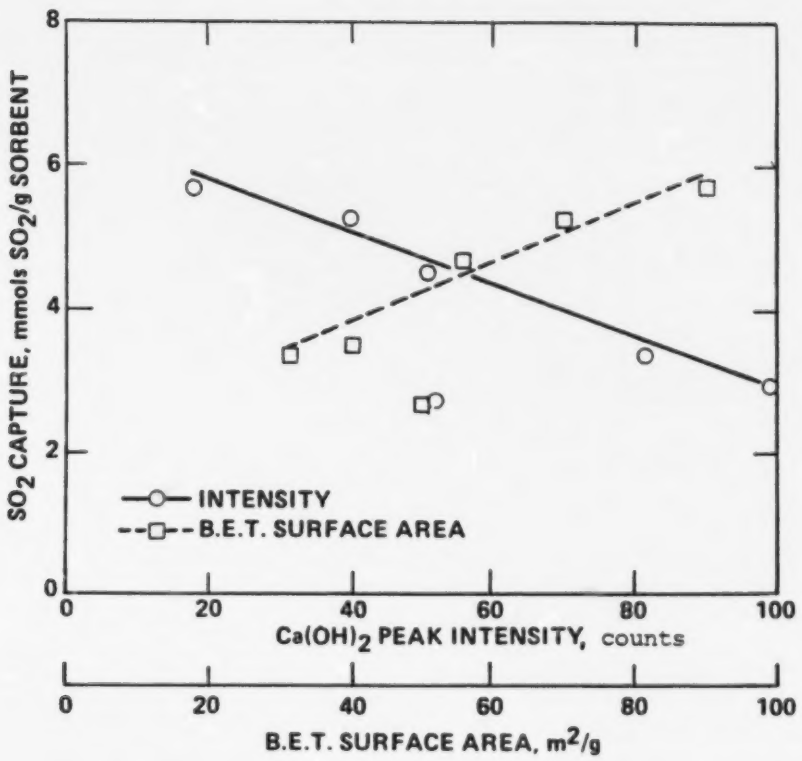


Figure 9. Correlation of the reactivity of diatomaceous earth (MN-53)/CaO sorbents with the B.E.T. surface area and with the amount of free $Ca(OH)_2$ detected by x-ray diffraction.

TABLE 1. CRYPTOCRYSTALLINE SILICA/$Ca(OH)_2$ SORBENTS TESTED IN THE SAND-BED REACTOR

| No. | Trade Name | Mineral | Vendor | CRYPTOCRYSTALLINE SILICA | | | | CRYPTOCRYSTALLINE SILICA/CaO SORBENT[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | B.E.T. Surface Area [$m^2/g$] | Composition [Weight %] CaO | $SiO_2$ | $Al_2O_3$ | B.E.T. Surface Area [$m^2/g$] | Conversion[b] [mols $SO_2$/mol $Ca(OH)_2$] | $SO_2$ Capture[b] [mmols $SO_2$/g of Sorbent] |
| 1 | MN-53 | Natural Diatomaceous Earth | Eagle-Picher Industries, Inc. | 56 | 0.9 | 83.7 | 5.6 | 90 | 0.84 | 5.68 |
| 2 | Filter Gel | Natural Diatomaceous Earth | Johns-Manville Products Corporation | 90 | 0.5 | 87.0 | 3.0 | 104 | 0.68 | 4.58 |
| 3 | Kenite 108 | Natural Diatomaceous Earth | Witco Chemical Corporation | 40 | N/A[c] | N/A | N/A | 45 | 0.62 | 4.19 |
| 4 | FFFF Pumice | Pumice | Charles F. Hommedieu, Inc., & Sons | N/A | N/A | N/A | N/A | 37 | 0.42 | 2.82 |
| 5 | FF Vulcan | Pumice | Charles B. Chrystal Company | N/A | Trace | 72.0 | 12.5 | N/A | 0.29 | 1.94 |
| 6 | Empire White | Pumice | Empire White Products, Inc. | N/A | N/A | N/A | N/A | N/A | 0.28 | 1.83 |
| 7 | Cream Tripoli | Tripoli | Charles B. Chrystal Company | N/A | None | 97.5 | 0.65 | 25 | 0.28 | 1.90 |
| 8 | Rose Tripoli | Triploli | Charles B. Chrystal Company | N/A | None | 94.4 | 2.7 | 20 | 0.25 | 1.69 |
| 9 | Hess Pumice | Pumice | Hess Pumice Products | N/A | 0.8 | 70.0 | 14.2 | N/A | 0.24 | 1.60 |

[a] All sorbents slurried at a weight ratio of cryptocrystalline silica/CaO of 1:1; slurrying conditions: temperature = 90°C, time = 4 h

[b] In the sand-bed reactor after 1 h exposure to 1000 ppm $SO_2$; conditions in the sand bed: temperature = 64°C, relative humidity = 60%

[c] N/A = Not Available

TABLE 2. CLAY/CaO SORBENTS TESTED IN THE SAND-BED REACTOR

| No. | Trade Name | Mineral | Vendor | CLAY | | | | CLAY/CaO SORBENT[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | B.E.T. Surface Area [$m^2/g$] | Composition [Weight %] CaO | $SiO_2$ | $Al_2O_3$ | B.E.T. Surface Area [$m^2/g$] | Conversion[b] [mols $SO_2$/mol $Ca(OH)_2$] | $SO_2$ Capture[b] [mmols $SO_2/g$ of Sorbent] |
| 1 | Bentonite 149 | Montmorillonite | Whittaker, Clark & | N/A | 0.1-1 | 58-64 | 18-21 | 24 | 0.76 | 5.14 |
| 2 | Filtrol 105 | Montmorillonite | Harshaw/Filtrol | 330 | d | e | f | 38 | 0.59 | 4.01 |
| 3 | Filtrol 13 | Montmorillonite | Harshaw/Filtrol | 300 | d | e | f | 38 | 0.57 | 3.84 |
| 4 | ASP 400 | Aluminum Silicate | Engelhard Corporation | N/A | 0.03 | 45.4 | 38.5 | 19 | 0.54 | 3.67 |
| 5 | None | Na-Ca-Montmorillonite | Ward's Natural Science Establishment | N/A | N/A | N/A | N/A | N/A | 0.48 | 2.88 |
| 6 | Filtrol 4 | Montmorillonite | Harshaw/Filtrol | 280 | d | e | f | 54 | 0.47 | 3.20 |
| 7 | Filtrol 20 | Montmorillonite | Harshaw/Filtrol | 295 | d | e | f | N/A | 0.46 | 3.08 |
| 8 | Volclay 325 | Na-Montmorillonite | American Colloid Company | N/A | 0.65 | 63.0 | 21.0 | 35 | 0.43 | 2.88 |
| 9 | None | Kaolinite | Ward's Natural Science Establishment | N/A | N/A | N/A | N/A | N/A | 0.43 | 2.90 |
| 10 | None | Hectonite | Ward's Natural Science Establishment | N/A | N/A | N/A | N/A | 40 | 0.42 | 2.81 |
| 11 | None | Na-Montmorillonite | Ward's Natural Science Establishment | N/A | N/A | N/A | N/A | N/A | 0.39 | 2.64 |
| 12 | Bentonite | Montmorillonite | Fisher Scientific Company | N/A | N/A | N/A | N/A | N/A | 0.39 | 2.62 |
| 13 | King's Mountain Clay | Kaolinite | King's Mountain Mica Company | N/A | Trace | 45.0 | 35.0 | 21 | 0.38 | 2.54 |
| 14 | Southern Bentonite | Ca-Montmorillonite | Whitehead Brothers | N/A | 1.2-3.5 | 56-59 | 18-21 | N/A | 0.37 | 2.50 |

(continued)

TABLE 2. CLAY/CaO SORBENTS TESTED IN THE SAND-BED REACTOR (concluded)

| No. | Trade Name | Mineral | Vendor | CLAY | | | | CLAY/CaO SORBENT[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | B.E.T. Surface Area [$m^2/g$] | Composition [Weight %] CaO | $SiO_2$ | $Al_2O_3$ | B.E.T. Surface Area [$m^2/g$] | Conversion[b] [mols $SO_2$/mol $Ca(OH)_2$] | $SO_2$ Capture[b] [mmols $SO_2/g$ of Sorbent] |
| 15 | Acidic Clay | Kaolinite | Unimin, Inc. | N/A | N/A | N/A | N/A | 32 | 0.36 | 2.44 |
| 16 | Bentonite 660 | Montmorillonite | Whittaker, Clark & Daniels | N/A | 0.1-1 | 58-64 | 18-21 | N/A | 0.35 | 2.39 |
| 17 | Burgess No. 17 | Aluminum Silicate | Burgess Pigment | N/A | N/A | 45.0 | 38-40 | N/A | 0.32 | 2.16 |

[a] All sorbents slurried at a weight ratio of clay/CaO of 1:1; slurrying conditions: temperature = 90°C, time = 4 h

[b] In the sand-bed reactor after 1h exposure to 1000 ppm $SO_2$; conditions in the sand bed: temperature = 64°F, relative humidity = 60%

[c] N/A = Not Available

[d] Between 0.1 and 1% CaO

[e] Between 55 and 70% $SiO_2$

[f] Between 18 and 25% $Al_2O_3$